

Synthesis and Properties of Polyamides and Polyesters Containing 2,2-Di-2'-thienylpropane Links

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Abstract : Series of polyamides and polyesters containing 2,2-di-2'-thienylpropane links were synthesized by the interfacial polycondensation of 2,2-di-(5-carbonylchloro-2-thienyl) propane with various diamines or diols. And the structures of these polymers were identified by infrared spectroscopy. Characteristic absorption bands of polyamides appeared at $3380\text{--}3240\text{cm}^{-1}$ (NH stretching), $1670\text{--}1640\text{cm}^{-1}$ (amide I band), and $1560\text{--}1540\text{cm}^{-1}$ (amide II band) and that of polyesters was observed at $1750\text{--}1720\text{cm}^{-1}$ (carbonyl stretching of ester group). The resulting polyamides had inherent viscosities in the range of $0.25\text{--}0.69\text{ dl/g}$ and those of polyesters were $0.12\text{--}0.33\text{ dl/g}$. And polyamides were obtained in higher yields than polyesters. Although most of the polyamides were soluble in polar solvents, polyesters were quite insoluble in common organic solvents. These polymers revealed relatively good thermal stability. The TGA data showed 5% weight losses of polyamides at $257\text{--}383^\circ\text{C}$ and those of polyesters at $244\text{--}308^\circ\text{C}$.

1. INTRODUCTION

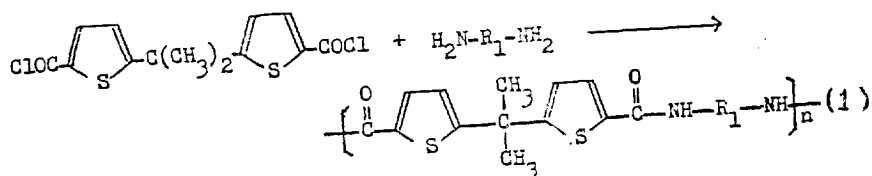
Preparations of linear polyamides and polyesters those contain heterocyclic links such as pyridine¹⁻⁹, pyrazine^{8,10}, piperidine³, furan^{1,3,4,8,11-16}, tetrahydrofuran^{8,13,17}, thiophene^{1,3,4,8,12,18}, and tetrahydrothiophene⁸ have been reported by several workers in the last two decades. The research in this field, in general, has aimed at obtaining products with properties comparable to those of well-known aromatic counterparts prepared with monomers such as terephthalic acid¹, bisphenol-A^{19,20}, and *m*-phenylenediamine^{18,21}, etc.

The vast majority of these studies describe the use of 2,5-disubstituted furan and thioph-

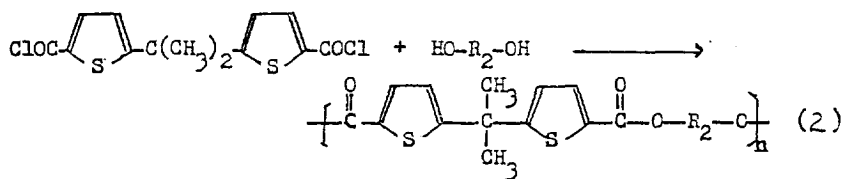
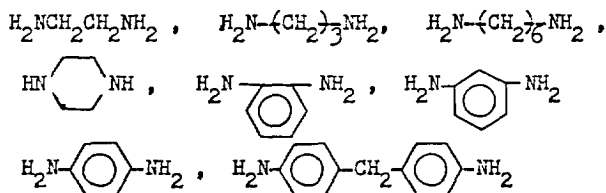
ene, since these five-membered heterocyclics reveal aromaticity²². The most widely used starting materials for these synthesis have been 2,5-furandicarboxylic acid and 2,5-thiophenedicarboxylic acid. Other types of monomers such as 2,5-bis(hydroxymethyl)furan^{13,19},²¹ and 2,5-bis(aminomethyl)thiophene^{18,21} were also used.

Virtually all the techniques of polycondensation including bulk¹, solution^{13,19,20}, and interfacial mixing^{1,18} have been tried with a variety of catalysts^{13,19,20} in an effort to optimize the properties of the polymers.

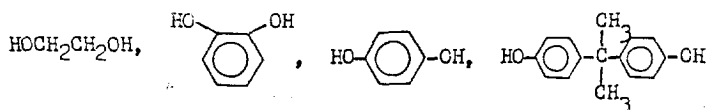
Although there is a great disagreement among data obtained by different authors dealing with a given system, most of these furan and



where $\text{H}_2\text{N}-\text{R}_1-\text{NH}_2$ is



where $\text{HO}-\text{R}_2-\text{OH}$ is



thiophene polycondensates are more sensitive to thermal and oxidative degradation than their benzene analogues^{1,15},

It is expected that disubstituted dithienyl derivatives would produce relatively good thermally stable polymers owing to their inflexible chains. Few, however, have reported the synthesis of polymers those contain dithienyl derivatives.

The present work was undertaken to synthesize polyamides and polyesters by the reaction of 2,2-di-(5-carbonylchloro-2-thienyl) propane with various diamines [eq.(1)] or diols [eq.(2)] and to investigate some of their properties.

2. EXPERIMENTAL

2-1. Materials

Thiophene(Aldrich Chemical Co., gold label; 99%, bp;84°C), bromine(Kanto Chemical Co., EP-grade, bp;58-59°C), Thionyl chloride, aniline, piperazine(Aldrich Chemical Co., 99%, mp;108-110°C), phenol and catechol were used without further purifications.

1,3-Propylenediamine(Aldrich Chemical Co., 99%, bp;120°C) was purified by azeotropic distillation with toluene. Ethylene glycol(Katayama Chemicals, LTD., 90%) was dried over calcium sulfate and distilled under reduced pressure; bp 107-108°C/4mmHg.

Hexamethylenediamine(Wako pure Chemical Ind. Inc., 98%, mp; 39-40°C), *m*-phenylenediamine(99%, mp;64-66°C), and *p*-phenylenediamine(99%, mp;138-140°C) were used after recrystallization from ethanol.

o-Phenylenediamine(mp;158°C) was purified

by recrystallization from 1% sodium hyposulfite aqueous solution. 4,4'-Methylenedianiline (mp; 158°C) and hydroquinone (Wako Pure Chemical Ind. Inc., 99%, mp; 172-173°C) were recrystallized from benzene. Bisphenol-A (Aldrich Chemical Co., 97%, mp; 153-156°C) was recrystallized from 50% acetic acid.

All the other reagents and solvents used were purified in the usual manner^{23,24},

2-2. Instruments and Measurements

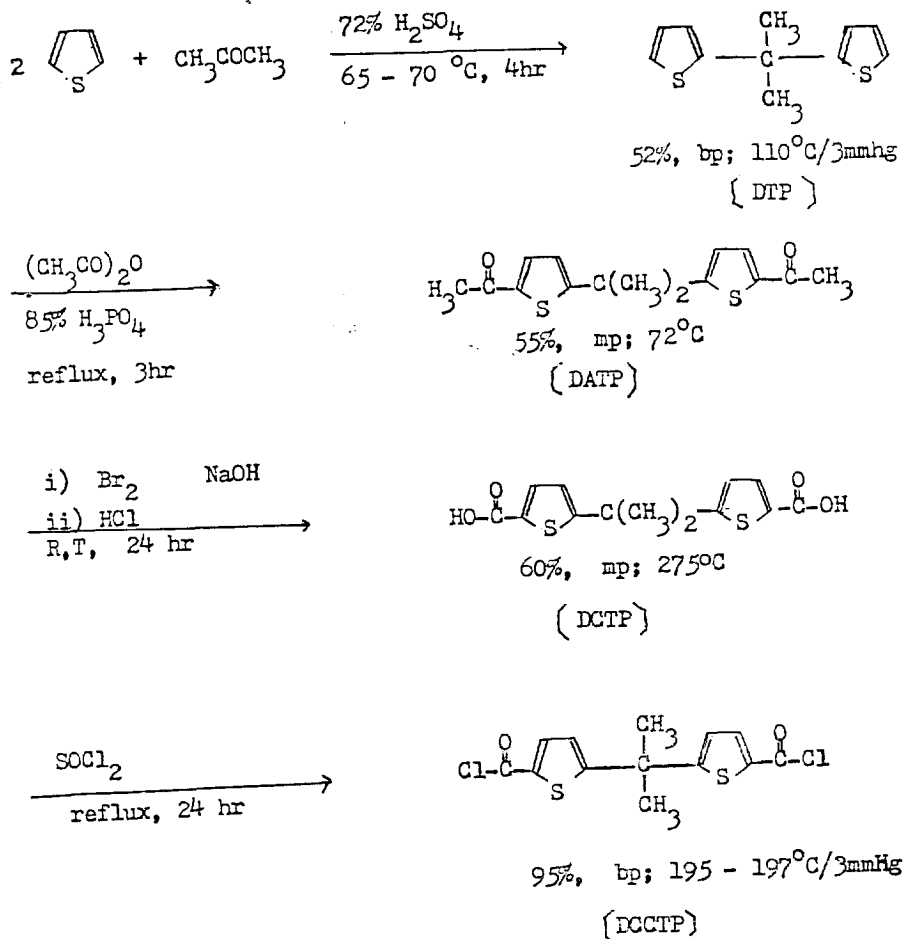
Infrared (IR) spectra were obtained on a Perkin-Elmer 267 Spectrophotometer with a KBr disk or liquid cell. Proton Nuclear Magnetic Resonance (¹H NMR) spectra were recorded

on a Varian T60A Spectrometer. The chemical shifts (δ) are given in ppm with tetramethylsilane (TMS) as the external standard.

Melting points of the polymers were determined on Du Pont model 910 DSC and 990 Thermal Analyzer. Thermogravimetric analyses (TGA) were performed in nitrogen at a heating rate of 10°C/min with a Perkin-Elmer TGS-1 Thermobalance.

Viscosity measurements were made with 0.5% solutions of the polymers in distilled m-cresol or in 95% sulfuric acid at 30°C.

2-3. Preparation of 2,2-Di-(5-carbonyl-2-thienyl) propane (DCCTP)



Scheme 1. Preparation of DCCTP.

2,2-Di-(5-carbonylchloro-2-thienyl) propane [DCCTP] was prepared by the electrophilic substitution reaction of thiophene with acetone in the presence of acid catalyst, followed by acetylation, oxidation by bromoform reaction, and finally thionyl chloride treatment. The overall reaction procedure is represented in scheme 1.

2-3-1. 2,2-Di-2'-thienylpropane [DTP]

DTP was prepared according to the slightly modified process of Schick and Crowley's method²⁵. In a flask equipped with a stirrer, 84g (1mole) of thiophene was mixed with 126g of 72% sulfuric acid at 65°C. While vigorously stirring, 29g (0.5mole) of acetone was added dropwise during 10 min. When the addition was completed, the temperature was raised to 70°C. After 4hr stirring, 200ml of water was added to the flask. The crude product was several times extracted from the reaction mixture with chloroform. The combined extracts were washed with 10% sodium carbonate, then water, and dried over anhydrous calcium chloride. After distillation under reduced pressure, 54.1g (52%) of DTP were obtained. bp; 110°C/3mmHg, IR(neat) 3100-3080 2980 1365 825cm⁻¹, ¹H NMR(CCl₄) δ 1.81(s, 6H, CH₃) 6.65-6.95(m, 4H, thiophene ring proton). Lit.²⁵; 47%, bp; 86°C/0.3mmHg.

2-3-2. 2,2-Di-(5-acetyl-2-thienyl)propane [DATP]

In a flask equipped with a stirrer and a reflux condenser, 41.6g (0.2mole) of DTP was dissolved in 153g (1.5moles) of acetic anhydride. While stirring, 10g of 85% orthophosphoric acid was added and the mixture was refluxed for 3hr. The reaction mixture was poured into 200g of icewater and stirred until the excess acetic anhydride had completely hydrolyzed. The organic materials were extracted with chloroform. The combined extracts were then

dried over calcium chloride and the low boiling components were distilled off under reduced pressure. When 200ml of ethanol-petroleum ether(1:1) mixture was added to the concentrated purple colored residue, the crude product was precipitated. The precipitate was then recrystallized again from ethanol-petroleum ether(1:1) mixed solvent. 32.1g (55%) of DATP were obtained. mp; 72°C, IR(KBr): 30 90 2980 1660 ($\nu_{C=O}$) 1360 810cm⁻¹, ¹H NMR(CCl₄); 1.82(s, 6H, bridge CH₃) 2.43(s, 6H, OC H₃) 6.80-7.40(d. of d., 4H, thiophene ring proton). Lit.²⁶; 60%, mp; 75-75.5°C.

2-3-3. 2,2-Di-(5-carboxy-2-thienyl) propane [DCTP]

DCTP was prepared via the bromo form reaction of DATP according to the Badger, Rodda, and Sasse' procedure²⁸. 60%, mp; 275°C, IR(KBr); 1675($\nu_{C=O}$ of acid) 1360 820cm⁻¹, ¹H NMR(DMSO-d₆); δ 1.82(s, 6H, bridge CH₃) 7.00-7.58 (d. of d., 4H, thiophene ring proton). Lit. (107). 62%, mp; 275-277°C.

2-3-4. 2,2-Di-(5-carbonylchloro-2-thienyl) propane [DCCTP]

In a flask fitted with a reflux condenser and a stirrer, 26.9g (0.1mole) of DCTP was placed. While stirring, 40ml of thienyl chloride was added dropwise for 30min and refluxed for 24 hr. The dark solution was allowed to cool and the excess thionyl chloride was evaporated off. After distillation under reduced pressure, 31.6g (95%) of DCCTP were obtained. bp; 195-197°C/3 mmHg, IR(neat) Fig. 1; 1690($\nu_{C=O}$ of acid chloride) 1370cm⁻¹, ¹H NMR(CCl₄) Fig. 1, δ 2.0(s, 6H, bridge CH₃) 7.05-7.85(d. of d., 4H, thiophene ring proton).

2-4. Polymerization

2-4-1. Synthesis of Polyamides Containing 2,2-Di-2'-thienylpropane Links

A typical procedure for the synthesis of polyamides is as follows. A solution of the 1.00g

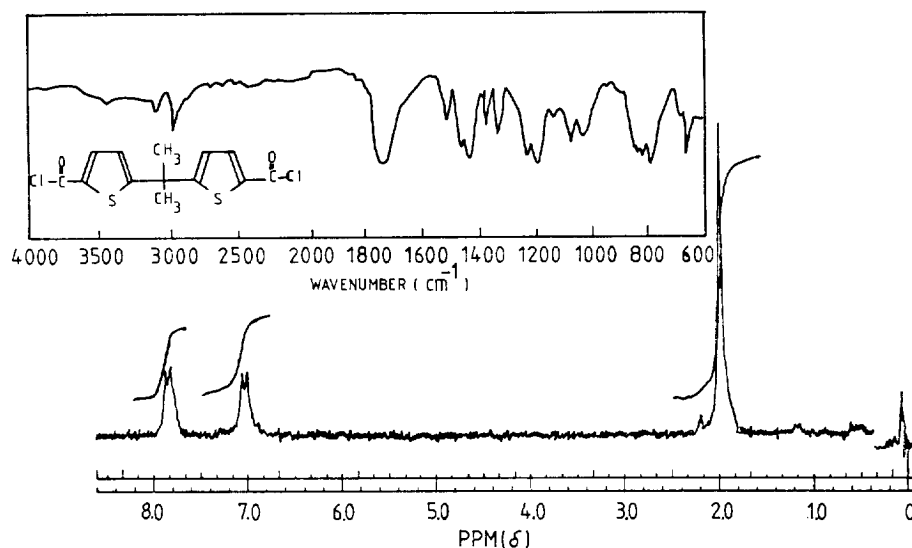


Fig. 1. IR and ^1H NMR spectra of 2,2-di-(5-carboxylchloro-2-thienyl) propane (DCCTP)

(3mmoles) of DCCTP in 30ml of methylene chloride was added to a solution of 0.324g(3 mmole) of *p*-phenylenediamine in 30ml of 0.2N sodium hydroxide aqueous solution for 10 min. After completing the addition, the reaction mixture was vigorously stirred at 0°C for 3hr. The precipitated polymer was filtered, then washed consecutively with water and methylene chloride and dried in vacuo at 60°C for 24hr. The yield of light brown colored polymer (I-g) was 1.146g(94%). The inherent viscosity measured at a concentration of 0.5g/dl in *m* cresol at 30°C was 0.25dl/g.

2-4-2. Synthesis of Polyesters containing 2,2-Di-2'-thienylpropane Links

A typical polyesterification was performed as follows: 0.684g(3mmoles) of bisphenol-A was dissolved in 30 ml of 0.2N sodium hydroxide solution. After the addition of 4 drops of aqueous 60% triethylbenzylammonium chloride, the solution was cooled to 0°C . To this was added a solution of 1,000g(3mmoles) of DCC-TP in 30 ml of methylene chloride with rapid

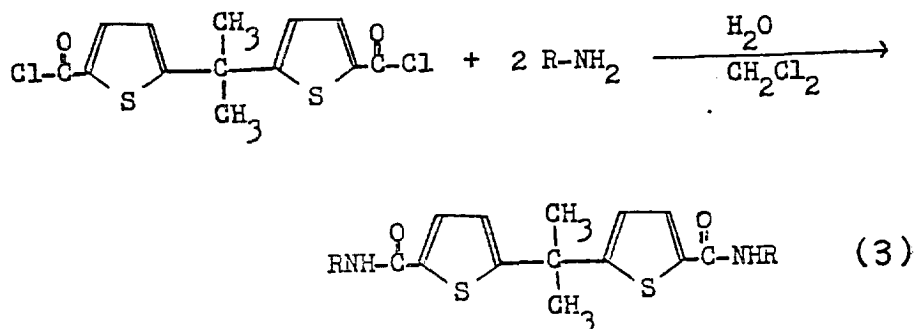
stirring for 10 min. After 3hr stirring, the polymer cake was filtered and washed several times with methylene chloride and water. After drying in vacuo at 60°C for 24hr, 1,318g (90%) of light yellow-colored polymer(II-d) were obtained. The inherent viscosity measured at a concentration of 0.5g/dl in 95% sulfuric acid was 0.33dl/g.

3. RESULTS AND DISCUSSION

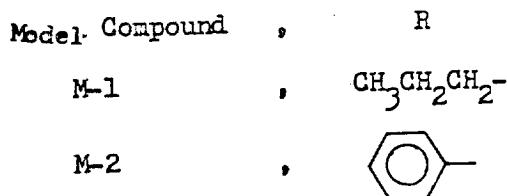
3-1. Model Reaction

To study the general scope of the polycondensation reaction of DCCTP towards various diamines and to identify the structures of polyamides, model compounds were synthesized by the condensation reaction of DCC-TP with *n*-propylamine or aniline [eq.(3)].

The general reaction procedure is as follows: 6mmoles of *n*-propylamine(0.36g) or aniline(0.56g) was dissolved in 30 ml of 0.2N sodium hydroxide solution and the solution was cooled to 0°C . To this was added a solution of 1.00g (3mmoles) of DCCTP in 30ml of methylene



where



chloride with rapid stirring for 10 min. After 1 hr, the precipitated crude product was filtered and washed several times with water and methylene chloride. The model compound was then dried in vacuo at 60°C for 24hr. The model compounds were characterized by IR and ^1H NMR spectra. The results of the model reaction are summarized below.

2,2-Di-(5-propylamido-2-thienyl) propane[M-1]. 95%, white platelets, mp:198°C, IR(KBr), Fig. 2 3,320(ν_{NH}) 3,080 2,960 1,630($\nu_{\text{C=O}}$) 1,550 (amide II band) 1,370 810 cm^{-1} , ^1H NMR(DMSO- d_6) Fig. 2: δ 0.75(t, 6H, C-CH₃) 1.50 (m, 4H, C-CH₂-C) 1.70(s, 6H, bridge CH₃) 3.20 (m, 4H, N-CH₂-C) 6.90 and 7.30(d. of d., 4H, thiophene ring proton).

2,2-Di-(5-phenylamino-2-thienyl) propane[M-2]. 89%, white platelets, mp; 222°C, IR(KBr) Fig. 3; 3,300(ν_{NH}) 3,060 2,970 1,640($\nu_{\text{C=O}}$) 1,540 1,370 810 cm^{-1} , ^1H NMR(DMSO- d_6): δ 1.70 (s, 6H, bridge CH₃) 6.90-7.85(m, 14H, aromatic proton) 10.20(s, 2H, CONH).

As shown in Fig. 2, characteristic IR absorp-

tion bands were observed at 3,320-3,300 cm^{-1} (NH stretching), 1,640-1,630 cm^{-1} (C=O stretching of amide, amide I band), and 1,550-1,540 cm^{-1} (amide II band) and also the characteristic N-H peak appeared at 8.30-10.20 ppm in ^1H NMR spectra.

In addition to methylene chloride, other organic solvents such as chloroform, benzene, and *m*-xylene were also tested. However, no appreciable increase in yield was observed.

Model compounds were readily soluble in polar solvents such as DMF, DMSO, and *m*-cresol etc.

3-2. Synthesis and Identification of Polyamides and Polyesters those contain 2,2-Di-2'-thienylpropane Links

On the basis of the results of model reaction, interfacial polycondensation reaction of DCCTP with various diamines or diols was carried out to produce polyamides and polyesters those contain 2,2-di-2'-thienylpropane links. In case of polyesterification, triethylbenzylammonium chloride was used as a phase

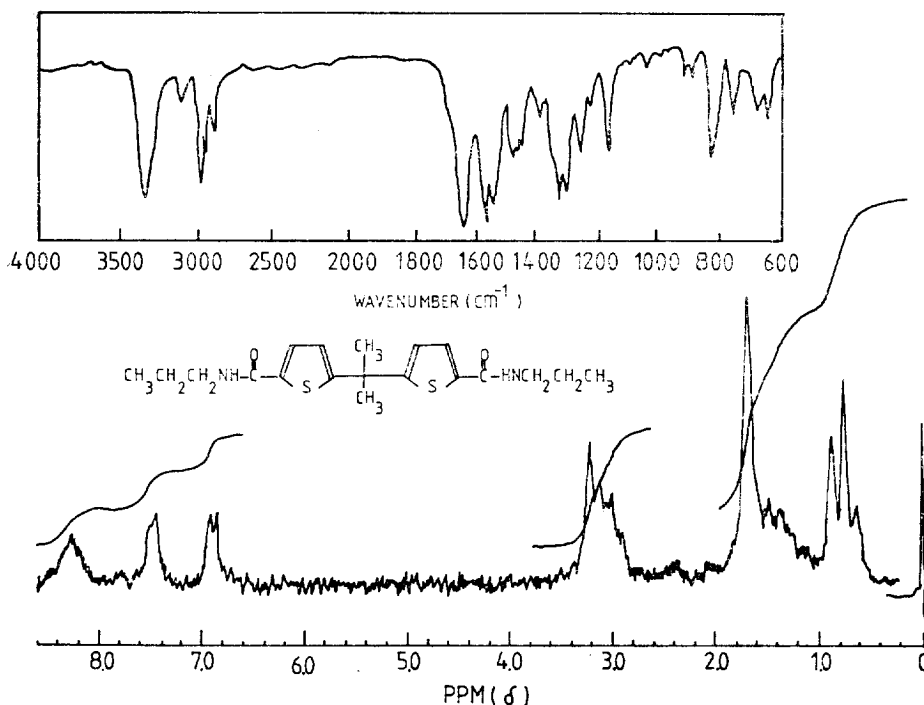


Fig. 2. IR and ^1H NMR spectra of 2,2-di-(5-propylamido-2-thienyl) propane (model compound [M-1]).

transfer catalyst^{27,28}. It has been stated that quaternary ammonium salts play the role of phase transfer catalyst in interfacial mixing of acid chlorides and alcohols as represented in scheme 2.

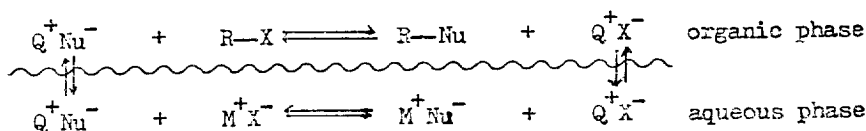
The conversion and degree of polymerization of polyamides were, in general, higher than those of polyesters. That is, the yield and inherent viscosity of polyamides were in the range of 85-95% and 0.25-0.69 dl/g, respectively. Side reactions such as cyclization may cause the exceptional low molecular weight

polymer in *o*-phenylenediamine. In contrast to polyamides, inherent viscosity of polyesters was 0.12-0.33 dl/g and conversion correspondingly in the range of 45-90%. Relatively lower nucleophilicity of diols probably limits the effective growing of the polymer chains.

The results of polymerization are summarized in Table 1.

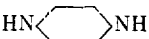



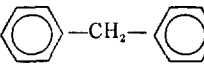


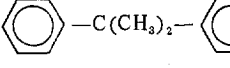
The structures of polymers were identified by IR spectroscopy and spectra of polyamides were quite similar to those of model compounds. The IR spectra of model compound M-2

(Scheme 2)



Synthesis and Properties of polyamide and Polyesters Containing 2,2-Di-2'-thienylpropane Links

Table 1. Synthesis of Polyamides and Polyesters Those Contain 2,2-Di-2'-Thienylpropane Links by Interfacial Polycondensation of DCCTP^a with Various Diamines and Diols

Polymer	Diamine or Diol	Color	Yield(%)	η_{inh}^b (dl/g)
Polyamides				
I -a	$H_2NCH_2CH_2NH_2$	LY	90	0.51
I -b	$H_2NCH_2CH_2CH_2NH_2$	W	92	0.47
I -c	$H_2N-(CH_2)_6-NH_2$	LY	93	0.40 ^c
I -d		LY	95	0.69
I -e	H_2N-  $-NH_2$	LY	85	0.09
I -f	H_2N-  $-NH_2$	DB	89	0.36
I -g	H_2N-  $-NH_2$	LY	94	0.25
I -h	H_2N-  $-NH_2$	Y	88	0.62
Polyesters				
II -a	$HOCH_2CH_2OH$	LB	45	0.26 ^c
II -b	$HO-$  $-OH$	DB	62	0.12 ^c
II -c	$HO-$  $-OH$	DB	71	0.14 ^c
II -d	$HO-$  $-OH$	LY	90	0.33 ^c

a; 2,2-Di-(5-carbonylchloro-2-thienyl) propane.

b; Measured at a concentration of 0.5g/dl in m-cresol at 30°C.

c; Measured at a concentration of 0.5g/dl in 95% H_2SO_4 at 30°C.

W; white, Y; yellow, LY; light yellow, LB; light brown, DB; dark brown.

and polyamide 1-f are compared in Fig. 3. As shown in Fig. 3, strong absorption bands appeared at $3380-3,240cm^{-1}$ (NH stretching), $1,670-1,640cm^{-1}$ (amide I band), $1,560-1,540cm^{-1}$ (amide II band), and $815cm^{-1}$ (thiophene ring breathing). Also the characteristic carbonyl absorption band of ester group was found at $1,750-1,720cm^{-1}$ in IR spectra of polyesters as can be seen in Fig. 4 characteristic IR absorption bands of polyamides and polyesters are listed in Table 2.

3-3. Properties of Polyamides and Polyesters

3-3-1. Solubility

Solubility test of the polymers obtained in this research was performed for powdery samples in excess solvent. The solubility data are summarized in Table 3. All polymers were soluble in concentrated sulfuric acid. And most of the polyamides were soluble in polar solvents such as DMF, m-cresol, DMSO, and trifluoroacetic acid. However as shown in Table 3, polyesters were quite insoluble in common or-

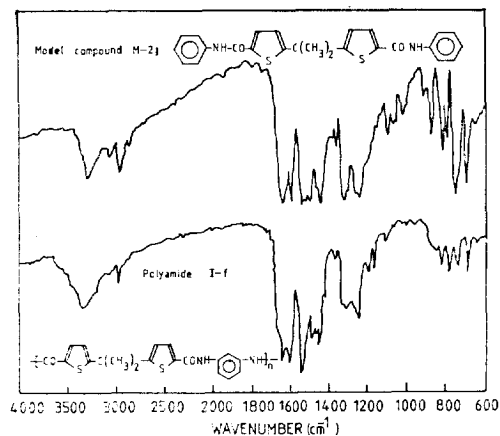


Fig. 3. IR Spectra of model compound M-2 and polyamide I-f.

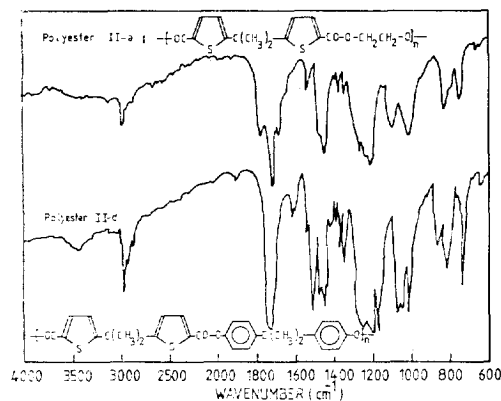


Fig. 4. IR Spectra of polyesters; polymer II-a and II-d.

ganic solvents.

3-3-2. Thermal Stability

The thermal stability of these polyamides and polyesters was evaluated by thermogravimetric analysis(TGA) as well as differential scanning calorimetry(DSC). Typical TGA curves of these polymers are shown in Fig. 5 and thermal stability data are listed in Table 4. Most of these polyamides and polyesters were infusible. An examination of the thermal stability data revealed that polyamides were more thermally stable than polyesters. Polyamides exhibited 5% weight losses at 257-38

Table 2. Characteristic IR Absorption Band of Polyamides Polyesters^a

Polymer	IR absorption bands(cm ⁻¹)
I-a	3340-3280(ν_{NH}) 3080(ν_{CH} of aromatic) 2980(ν_{CH} of al-phatic) 1640(amide I) 1550(amide II) 1370 815
I-b	3360-3300 3080 2940 1640 1550 1545 1375 815
I-c	3360-3320 3080 2980 1640 1550 1370 815
I-d	3450-3420 3100-3060 2980 1640 1540 1370 815
I-e	3300-3240 3080 2980 1650 1540 1370 815
I-f	3380-3300 3090 2980 1650 1550 1370 815
I-g	3340-3240 3040 2980 1650 1550 1370 815
I-h	3350 3050 2980 1650 1550 1370 815
II-a	3100 2980 1720($\nu_{\text{C=O}}$ of ester) 1370 815
II-b	3100 2980 1740($\nu_{\text{C=O}}$) 1370 815
II-c	3100 2980 1750 1370 815
II-d	3100-3020 2980 1730 1370 815

^a Obtained in KBr pellet.

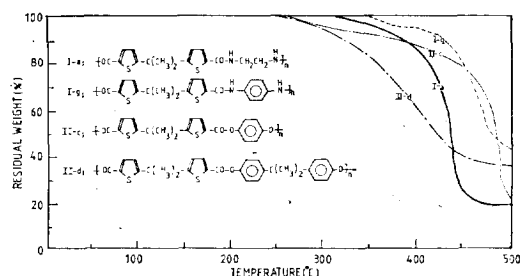


Fig. 5. Typical TGA curves of polyamides and polyesters; polyamide I-a, I-g, polyester II-c, and II-d.

3°C. On the other hand, 5%, weight losses in polyesters occurred in the range of 244-308°C. Intermolecular hydrogen bonding in polyamides may be responsible for this higher thermal stability.

Although these polyamides and polyesters those contain 2,2-di-2'-thienylpropane links show relatively good thermal stability, these polymers are still more sensitive to thermal degradation than their wellknown benzene counterparts.

Table 3. Solubility^a of Polyamides and Polyesters

Polymer	Solvent							
	DMF	DMSO	S.A	m-Cresol	TFA	AcOH	THF	MeOH
I -a	+-	++	+	++	++	-	-	-
I -b	+-	++	+	++	++	-	-	-
I -c	-	-	+	-	+-	-	-	-
I -d	-	-	++	++	++	-	-	-
I -e	++	++	++	++	++	-	-	-
I -f	++	++	++	++	++	+-	-	+-
I -g	++	++	++	-	-	-	-	-
I -h	+-	++	++	++	++	-	-	-
II -a	-	-	++	-	+-	-	-	-
II -b	-	-	++	-	-	-	-	-
II -c	-	-	++	-	+-	-	-	-
II -d	+-	-	++	++	++	-	++	-

^a ++; soluble, +-; soluble by heating, +-; partially soluble, -; insoluble.

Abbreviations: S.A; concentrated sulfuric acid, TFA; trifluoroacetic acid, THF; tetrahydrofuran, MeOH; methanol.

Table 4. Thermal Stability of Polyamides and Polyesters^a

Polymer	Tg ^b (°C)	PMT ^c (°C)	5% Weight loss(°C)	10% Weight loss(°C)	RW ^d at 500°C(%)
I -a	152	322	347	393	19.0
I -b	-	-	353	381	8.6
I -c	-	-	289	329	11.2
I -d	125(Tc)	305(dec.)	317	379	48.9
I -e	125	332(dec.)	325	330	16.9
I -f	125	382(dec.)	383	419	39.4
I -g	140	-	382	433	42.7
I -h	155	-	257	267	34.3
II -a	-	-	272	319	36.2
II -b	137(Tc)	-	257	321	45.0
II -c	140	-	244	308	37.5
II -d	-	-	308	387	22.3

^a Observed in TGA in nitrogen(10°C/min.).

^b Glass transition temperature: determined with DSC in nitrogen(10°C/min.).

^c Polymer melt temperature: determined with DSC under nitrogen(10°C/min.)

^d Residual Weight.

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